

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 307 564 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
21.02.1996 Bulletin 1996/08

(51) Int Cl.⁶: C11D 11/00, D06M 16/00

(21) Application number: 88110929.2

(22) Date of filing: 08.07.1988

(54) **Methods that introduce variations in color density into dyed cellulosic fabrics**

Verfahren zum Einbringen von Unterschieden der Farbdichte in gefärbten Cellulosematerialien

Méthodes pour introduire des variations de densité de couleur dans des matériaux cellulosiques teints

(84) Designated Contracting States:
BE DE ES FR GB GR IT LU NL SE

(30) Priority: 15.09.1987 US 96953

(43) Date of publication of application:
22.03.1989 Bulletin 1989/12

(60) Divisional application: 95100251.8

(73) Proprietor: ECOLAB INC.
St. Paul, Minnesota 55102 (US)

(72) Inventor: Olson, Lynne A.
Mendota Heights, Minnesota 55120 (US)

(74) Representative:
Malwald, Walter, Dr. Dipl.-Chem. et al
D-80336 München (DE)

(56) References cited:

- | | |
|-----------------|-----------------|
| EP-A- 0 206 418 | EP-A- 0 220 016 |
| US-A- 3 844 890 | US-A- 4 081 328 |
| US-A- 4 435 307 | US-A- 4 443 355 |
- G. Vanescini e.a., Biotechnol. Bioeng. 23(7), 1573-90 (1981)
 - Novo Enzymes: Celluclast (R), pamphlet No. B 153g-GB, June 1984 (Novo Industri A/S);
 - Novo Enzymes: Celluzyme TM, Pamphlet No. B 338c-GB, April 1987 (Novo Industri A/S)
 - Publication AF 187/3-GB, published 1983 by Novo Industri A/S
 - S. Hayashida e.a., Agric. Biol. Chem., 44(3), 481-487 (1980)
 - S. Hayashida e.a., Agric. Biol. Chem., 44 (8) 1721-1728 (1980)
 - M. Tschetkarov e.a., Monatshefte für Chemie, 98(5), 1916-29 (1967)
 - M.A. Hulme, Arch. Biochem. Biophys., 147(1), 49-54 (1971)
 - Plant & Cell Physiology, 17, 899-908 (1976); W.A. Wood e.a., eds. Biomass: Meth. in Enzymol., 160, Chapter 13 (1988)
 - M. Schulein, Methods in Enzymology, 60, 234-242 (1988)
 - Handbook of Practical Biotechnology, Boyce (1986)
 - Ghose, Pure & Applied Chemistry, 59(2), 257-268 (1987)

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

The invention relates to the manufacture of clothing from dyed cellulosic fabrics. More particularly, the invention relates to pumice-free processes used in the manufacture of a clothing item, preferably from denim fabric dyed with indigo, that can produce in a clothing item a distressed, "used and abused" appearance that is virtually indistinguishable from the appearance of "stone washed" clothing items made by traditional pumice processing.

Clothing made from cellulosic fabrics such as cotton and in particular indigo dyed denim fabrics have been common items of clothing for many years. Such clothing items are typically sold after they are sewn from sized and cut cloth. Such clothes and particularly denim clothing items are stiff in texture due to the presence of sizing compositions used to ease manufacturing, handling and assembling of the clothing items and typically have a fresh dark dyed appearance. After a period of wear, the clothing items, particularly denim, can develop in the clothing panels and on seams, localized areas of variations, in the form of a lightening, in the depth or density of color. In addition a general fading of the clothes can often appear in conjunction with the production of a "fuzzy" surface, some pucker in seams and some wrinkling in the fabric panels. Additionally, after laundering, sizing is substantially removed from the fabric resulting in a softer feel. In recent years such a distressed or "used and abused" look has become very desirable, particularly in denim clothing, to a substantial proportion of the public. To some extent, a limited pre-worn appearance, which has a uniform color density different than the variable color density in the typical stone-washed item, can be produced through prewashing or preshrinking processes.

The preferred methods for producing the distressed "used and abused" look involve stone washing of a clothing item. Stone washing comprises contacting a denim clothing item or items in large tub equipment with pumice stones having a particle size of about 2.5 to 25 cm (1 to 10 inches) and with smaller pumice particles generated by the abrasive nature of the process. Typically the clothing item is tumbled with the pumice while wet for a sufficient period such that the pumice abrades the fabric to produce in the fabric panels, localized abraded areas of lighter color and similar lightened areas in the seams. Additionally the pumice softens the fabric and produces a fuzzy surface similar to that produced by the extended wear of the fabric.

The 2.5 to 25 cm (1 to 10 inch) pumice stones and particulate pumice abrasion by-products can cause significant processing and equipment problems. Particulate pumice must manually be removed from processed clothing items (de-rocking) because they tend to accumulate in pockets, on interior surfaces, in creases and in folds. In the stone washing machine, the stones can cause overload damage to electric motors, mechanical damage to transport mechanisms and washing drums and can significantly increase the requirements for machine maintenance. The pumice stones and particulate material can clog machine drainage passages and can clog drains and sewer lines at the machine site. Further, the abraded pumice can clog municipal sewer lines, can damage sewage processing equipment, and can significantly increase maintenance required in municipal sewage treatment plants. These problems can add significantly to the cost of doing business and to the purchase price of the goods.

In view of the problems of pumice in stone washing, increasing attention has been directed to finding a replacement for stone washing in garment manufacture (see the Wall Street Journal, May 27, 1987, p. 1.). One avenue of investigation involves using a replacement stone such as a synthetic abrasive. In particular, ceramic balls such as those used in ball mills and irregular hard rubber pieces, which can be used without producing abraded by-products, have been experimented with in stone washing processes. These materials reduce the unwanted effects caused by particulate by-product pumice but do not significantly reduce machine damage caused by stones or the required maintenance on stone-containing laundry tubs. As a result, significant attention has been directed to producing a stone-free or pumice-free "stone washed" process that can produce a stone-washed denim look.

One disadvantage in pumice processing is that pumice cannot be used in tunnel washers, the largest commercial washing machines. Pumice cannot be circulated through the tunnel machines due to machine internal geometry. The use of larger-scale tunnel washers could significantly increase the productivity of the processes with the use of a stone or pumice-free composition that produces a genuine "stone-washed" look.

Barbesgarrrd et al, U.S. Pat. No. 4,435,307 teach a specific cellulase enzyme that can be obtained from Humicola insolens which can be used in soil removing detergent compositions. Martin et al, European Pat. Application No. 177,165 teach fabric washing compositions containing a surfactant, builders, and bleaches in combination with a cellulase composition and a clay, particularly a smectite clay. Murata et al, U.K. Pat. Application No. 2,095,275 teach enzyme containing detergent compositions comprising an alkali cellulase and typical detergent compositions in a fully formulated laundry preparation. Tai, U.S. Pat. No. 4,479,881 teaches an improved laundry detergent containing a cellulase enzyme in combination with a tertiary amine in a laundry preparation. Murata et al, U.S. Pat. No. 4,443,355 teach laundry compositions containing a cellulase from a cellulosomonas bacteria. Parslow et al, U.S. Pat. No. 4,661,289 teaches fabric washing and softening compositions containing a cationic softening agent and a fungal cellulase in conjunction with other typical laundry ingredients. Suzuki, U.K. Pat. Application No. 2,094,826 teaches detergent laundry compositions containing a cellulase enzyme.

EP-A-0 220 016 to NOVO INDUSTRI teaches to remove fibre debris produced by fabric wear from the surface of

the fabric, which debris gives the fabric a used or faded appearance, similar to the above-mentioned prior art.

EP-A-0 206 418 to Procter & Gamble discloses solid granular enzyme composition comprising, besides the enzyme, major amounts of buffer and filler components. The enzyme content is between 0.5 and 20 weight-%.

Dyed cellulosic clothing (such as denim) has been treated with desizing enzymes, detergents, bleaches, sour and softeners in prewashing and preshrinking processes. These variations are not intended to and do not duplicate the "stone-washed" look. A stone or pumice-free "stone-washed" process that produces the true stone-washed look has yet to be developed.

We have found that the "stone washed" appearance that takes the form of variations in local color density in fabric panels and seams of dyed cellulosic fabric, particularly in denim, clothing items can be substantially obtained using a stone or pumice-free process in which the clothing items are mechanically agitated in a tub with an aqueous treatment composition containing amounts of a cellulase enzyme that can degrade the cellulosic fabric and can release the fabric dye or dyes.

The aqueous treatment compositions are obtained by diluting a novel "stone-wash" liquid or solid concentrate consisting essentially of a cellulase enzyme and a diluent such as a compatible surfactant composition, a non-aqueous solvent or a solid-forming agent capable of suspending the cellulase without significant loss of enzymatic activity.

The use of cellulase enzyme preparations is known in laundry cleaning or detergent compositions. Such detergent compositions that are designed for soil removal typically contain surfactants (typically anionic), fillers, brighteners, clays, cellulase and other enzymes (typically proteases, lipases or amylases) and other laundry components to provide a full functioning laundry detergent preparation. The cellulase enzymes in such laundry preparations are typically used (at a concentration less than 500 to 900 CMC units per liter of wash liquor) for the purpose of removing surface fibrils or particles produced by fabric wear which tend to give the fabric a used or faded appearance. The cellulase enzymes in combination with the surfactants used in common laundry compositions for cleaning apparently can remove particulate soil and can restore the new appearance of clothing items. Such compositions are not known to introduce, into clothing, areas of variation in color density which can generally be undesirable in the laundry processing.

For the purpose of this invention, the terms "stone-washed appearance" and "variations in local color depth or density in fabric materials" are synonymous. The stone-washed appearance is produced in standard processing in fabric through an abrasion process wherein pumice apparently removes surface bound dye in a relatively small portion of the surface of a garment. Such an abraded area varies from the surrounding color or depth density and is substantially lighter in color. The production of such relatively small local areas of lightness or variation in color depth or density is the goal of both pumice containing stone washing processes in the prior art and Applicant's stone-free chemical treatment methods and compositions.

FIGURE 1 is a graph demonstrating the similarity in visual spectrophotometric character of authentic stone-washed jeans when compared to jeans produced by the methods of the invention.

The stone free "stone washed" methods of the invention involve contacting clothing items or denim fabric with an aqueous solution containing a major proportion of water; at least about 2,500 CMC units of a cellulase enzyme composition per liter of aqueous composition, and about 0 to 1000 parts of an enzyme-compatible surfactant per one million parts of the aqueous composition, and agitating the enzyme-treated fabric for a sufficient period of time to produce localized variations in color density through dye-removal from the fabric. The fabric items can be wet by the solution and agitated apart from the bulk aqueous liquors or can be agitated in the liquor. The aqueous treatment solution contains the cellulase enzyme and the cellulase compatible surfactant that increases the wetting properties of the aqueous treatment solution to enhance the cellulase effect.

The aqueous treatment solutions are typically prepared from a liquid or solid concentrate composition which can be diluted with water at appropriate dilution ratios to formulate the aqueous treatment solution. The "stone wash concentrate" compositions typically contain the cellulase enzyme and a diluent such as a compatible surfactant, a non-aqueous solvent or a solid-forming agent that can produce in a treatment liquor a suspension of the cellulase enzyme without significant enzyme activity loss.

The solid concentrate compositions typically comprise a suspension of the cellulase enzyme composition in a solid matrix. The solid matrixes can be inorganic or organic in nature. The solid concentrates can take the form of large masses of solid concentrate or can take the form of granular or pelletized composition. The solid concentrates can be used in commercial processes by placing the solid concentrate materials in dispensers that can direct a dissolving spray of water onto the solid or pellet material thereby creating a concentrated solution of the material in water which is then directed by the dispenser into the wash liquors contained in the commercial drum machines.

Enzymes are a group of proteins which catalyze a variety of typically biochemical reactions. Enzyme preparations have been obtained from natural sources and have been adapted for a variety of chemical applications. Enzymes are typically classified based on the substrate target of the enzymatic action. The enzymes useful in the compositions of this invention involve cellulase enzymes (classified as I.U.B. No. 3.2.1.4., EC numbering 1978). Cellulase are enzymes that degrade cellulose by attacking the C(1→4) (typically beta) glucosidic linkages between repeating units of glucose moieties in polymeric cellulosic materials. The substrate for cellulase is cellulose, and cellulose derivatives, which is a

high molecular weight natural polymer made of polymerized glucose. Cellulose is the major structural polymer of plant organisms. Additionally cellulose is the major structural component of a number of fibers used to produce fabrics including cotton, linen, jute, rayon and ramie, and others.

Cellulases are typically produced from bacterial and fungal sources which use cellulase in the degradation of cellulose to obtain an energy source or to obtain a source of structure during their life cycle. Examples of bacteria and fungi which produce cellulase are as follows: *Bacillus hydrolyticus*, *Cellulobacillus mucosus*, *cellulobacillus myxogenes*, *Cellulomonas* sp., *Cellvibrio fulvus*, *Cellvibrio vulgaris*, *Clostridium thermocellulaseum*, *Clostridium thermocellum*, *Corynebacterium* sp., *Cytophaga globulosa*, *Pseudomonas fluorescens* var. *cellulosa*, *Pseudomonas solanacearum*, *Bacterioides succinogenes*, *Ruminococcus albus*, *Ruminococcus flavefaciens*, *Sorandium composition*, *Butyrivibrio*, *Clostridium* sp., *Xanthomonas cyamopsidis*, *Sclerotium bataticola*, *Bacillus* sp., *Thermoactinomyces* sp., *Actinobifida* sp., *Actinomycetes* sp., *Streptomyces* sp., *Arthrobotrys superba*, *Aspergillus aureus*, *Aspergillus flavipes*, *Aspergillus flavus*, *Aspergillus fumigatus*, *Aspergillus fuchuenis*, *Aspergillus nidulans*, *Aspergillus niger*, *Aspergillus oryzae*, *Aspergillus rugulosus*, *Aspergillus sojae*, *Aspergillus sydwi*, *Aspergillus tamaril*, *Aspergillus terreus*, *Aspergillus unguis*, *Aspergillus ustus*, *Takamine-Cellulase*, *Aspergillus saitoi*, *Botrytis cinerea*, *Botryodiplodia theobromae*, *Cladosporium cucumerinum*, *Cladosporium herbarum*, *Coccospora agricola*, *Curvularia lunata*, *Chaetomium thermophile* var. *crophophila*, *Chaetomium thermophile* var. *dissitum*, *Sporotrichum thermophile*, *Taromyces amersonii*, *Thermoascus aurantiacus*, *Humicola grisea* var. *thermoidea*, *Humicola insolens*, *Malbranchea puichella* var. *sulfurea*, *Myriococcum albomyces*, *Stilbella thermophile*, *Torula thermophila*, *Chaetomium globosum*, *Dictyostelium discoideum*, *Fusarium* sp., *Fusarium bulbigenum*, *Fusarium equiseti*, *Fusarium lateritium*, *Fusarium lini*, *Fusarium oxysporum*, *Fusarium vasinfectum*, *Fusarium dimerum*, *Fusarium japonicum*, *Fusarium scirpi*, *Fusarium solani*, *Fusarium moniliforme*, *Fusarium roseum*, *Helminthosporium* sp., *Memnoniella echinata*, *Humicola fucoatra*, *Humicola grisea*, *Monilia sitophila*, *Monotospora brevis*, *Mucor pusillus*, *Mycosphaerella citrulina*, *Myrothecium verrucaria*, *Papulaspora* sp., *Penicillium* sp., *Penicillium capsulatum*, *Penicillium chrysogenum*, *Penicillium frequentans*, *Penicillium funiculosum*, *Penicillium janthinellum*, *Penicillium luteum*, *Penicillium piscarium*, *Penicillium soppi*, *Penicillium spinulosum*, *Penicillium turbatum*, *Penicillium digitatum*, *Penicillium expansum*, *Penicillium pusillum*, *Penicillium rubrum*, *Penicillium wortmanii*, *Penicillium variabile*, *Pestalotia palmarum*, *Pestalotiopsis westerdijkii*, *Phoma* sp., *Schizophyllum commune*, *Scopulariopsis brevicaulis*, *Rhizopus* sp., *Sporotrichum camis*, *Sporotrichum pruinatum*, *Stachybotrys atra*, *Torula* sp., *Trichoderma viride* (reesei), *Trichurus cylindricus*, *Verticillium albo atrum*, *Aspergillus cellulosa*, *Penicillium glaucum*, *Cunninghamella* sp., *Mucor mucedo*, *Rhizopus chinensis*, *Coremiella* sp., *Karlingia rosea*, *Phytophthora cactorum*, *Phytophthora citricola*, *Phytophthora parasitica*, *Pythium* sp., *Saprolegniaceae*, *Ceratocystis ulmi*, *Chaetomium globosum*, *Chaetomium indicum*, *Neurospora crassa*, *Sclerotium rolfsii*, *Aspergillus* sp., *Chrysosporium lignorum*, *Penicillium notatum*, *Pyricularia oryzae*, *Collybia velipes*, *Coprinus sclerotigenus*, *Hydnum henningii*, *Irpex lacteus*, *Polyporus sulphureus*, *Polyporus betreus*, *Polystictus hirsutus*, *Trametes vitata*, *Irpex consolus*, *Lentines lepideus*, *Poria vaporaria*, *Fomes pinicola*, *Lenzites styracina*, *Merulius lacrimans*, *Polyporus palstris*, *Polyporus annosus*, *Polyporus versicolor*, *Polystictus sanguineus*, *Poris vallantii*, *Puccinia graminis*, *Tricholome fumosum*, *Tricholome nudum*, *Trametes sanguinea*, *Polyporus schweinitzii* FR., *Conidiophora carebella*. Cellulase AP (Amano Pharmaceutical Co., Ltd.), Cellulosin™ AP (Ueda Chemical Co., Ltd.), Cellulosin™ AC (Ueda Chemical Co., Ltd.), Cellulase-Onozuka (Kinki Yakult Seizo Co., Ltd.), Pancellase™ (Kinki Yakult Seizo Co., Ltd.), Macerozyme™ (Kinki Yakult Seizo Co., Ltd.), Meicelase™ (Meiji Seika Kaisha, Ltd.), Celluzyme™ (Nagase Co., Ltd.), Soluble sclase (Sankyo Co., Ltd.), Sanzyme™ (Sankyo Co., Ltd.), Cellulase A-12-C (Takeda Chemical Industries, Ltd.), Toyo-Cellulase™ (Toyo Jozo Co., Ltd.), Driserase™ (Kyowa Hakko Kogyo Co., Ltd.), Luizyme™ (Luipold Werk), Takamine-Cellulase (Chemische Fabrik), Wallerstein-Cellulase (Sigma Chemicals), Cellulase Type I (Sigma Chemicals), Cellulase Serva™ (Serva Laboratory), Cellulase 36 (Rohm and Haas), Miles™ Cellulase 4,000 (Miles), R & H Cellulase 35, 36, 38 conc (Phillip Morris), Combizym™ (Nysco Laboratory), Cellulase (Makor Chemicals), Cellulast™, Celluzyme™, Cellucrust™ (NOVO Industry), and Cellulase (Gist-Brocades) can be used in the practising of this invention. Cellulase preparations are e.g. available from Accurate Chemical & Scientific Corp., Alltech, Inc., Amano International Enzyme, Boehringer Mannheim Corp., Calbiochem Biochems, Carolina Biol. Supply Co., Chem. Dynamics Corp., Enzyme Development, Div. Biddle Sawyer, Fluka Chem. Corp., Miles Laboratories, Inc., Novo Industrials (Biolabs), Plenum Diagnostics, Sigma Chem. Co., Un. States Biochem. Corp., and Weinstein Nutritional Products, Inc.

Cellulase, like many enzyme preparations, is typically produced in an impure state and often is manufactured on a support. The solid cellulase particulate product is provided with information indicating the number of international enzyme units present per each gram of material. The activity of the solid material is used to formulate the treatment compositions of this invention. Typically the commercial preparations contain from about 1,000 to 6,000 CMC enzyme units per gram of product.

A surfactant is included in the aqueous treatment compositions of the invention. The surfactant can increase the wettability of the aqueous solution promoting the activity of the cellulase enzyme in the fabric. The surfactant increases the wettability of the enzyme and fabric. The surfactant facilitates the exclusion of air bubbles from fabric surfaces and the enzyme preparation, and promotes contact between enzyme and fabric surface. The properties of surfactants are derived from the presence of different functional groups.

Surfactants are classified and well known categories including nonionic, anionic, cationic and amphoteric surfactants.

Nonionic surfactants are surfactants having no charge when dissolved or dispersed in aqueous medium. The hydrophilic tendency of nonionic surfactants is derived from oxygen typically in ether bonds which are hydrated by hydrogen bonding to water molecules. Hydrophilic moieties in nonionics can also include hydroxyl groups and ester and amide linkages. Typical nonionic surfactants include alkyl phenol alkoxylates, aliphatic alcohol alkoxylates, carboxylic acid esters, carboxylic acid amides, polyalkylene oxide random and block copolymers, and others.

Nonionic surfactants are generally preferred for use in this invention since they provide the desired wetting action and do not degrade the enzyme activity. Preferred nonionic surfactants include polymeric molecules derived from repeating units of ethylene oxide, propylene oxide, or mixtures thereof. Such nonionic surfactants include both homopolymeric, heteropolymeric, and block polymeric surfactant molecules. Included within the preferred class of nonionic surfactants are polyethylene oxide polymers, polypropylene oxide polymers, ethylene oxide-propylene oxide block copolymers, ethoxylated C₁₋₁₈ alkyl phenols, ethoxylated C₁₋₁₈ aliphatic alcohols, Pluronic™ surfactants, reverse Pluronic™ surfactants, and others.

Particularly preferred nonionics include: polyoxyethylene alkyl or alkenyl ethers having alkyl or alkenyl groups of a 10 to 20 average carbon number and having 1 to 20 moles of ethylene oxide added; polyoxyethylene alkyl phenyl ethers having alkyl groups of a 6 to 12 average carbon number and having 1 to 20 moles of ethylene oxide added; polyoxypropylene alkyl or alkenyl ethers having alkyl groups or alkenyl groups of a 10 to 20 average carbon number and having 1 to 20 moles of propylene oxide added; polyoxybutylene alkyl or alkenyl ethers having alkyl groups of alkenyl groups of a 10 to 20 average carbon number and having 1 to 20 moles of butylene oxide added; nonionic surfactants having alkyl groups or alkenyl groups of a 10 to 20 average carbon number and having 1 to 30 moles in total of ethylene oxide and propylene oxide or ethylene oxide and butylene oxide added (the molar ratio of ethylene oxide to propylene oxide or butylene oxide being 0.1/9.9 to 9.9/0.1); or higher fatty acid alkanolamides or alkylene oxide adducts thereof. Less preferred surfactants include anionic, cationic and amphoteric surfactants.

Anionic surfactants are surfactants having a hydrophilic moiety in an anionic or negatively charged state in aqueous solution. Commonly available anionic surfactants include carboxylic acids, sulfonic acids, sulfuric acid esters, phosphate esters, and salts thereof.

Cationic surfactants are hydrophilic moieties wherein the charge is cationic or positive when dissolved in aqueous medium. Cationic surfactants are typically found in amine compounds, oxygen containing amines, amide compositions, and quaternary amine salts. Typical examples of these classes are primary and secondary amines, amine oxides, alkoxylated or propoxylated amines, carboxylic acid amides, alkyl benzyl dimethyl ammonium halide salts and others.

Amphoteric surfactants which contain both acidic and basic hydrophilic structures tend to be of reduced utility in most fabric treating processes.

Solvents that can be used in the invention are liquid products that can be used for dissolving or dispersing the enzyme and surfactant compositions of the invention. Because of the character of the preferred nonionic surfactants, the preferred solvents are oxygen containing solvents such as alcohols, esters, glycol, glycol ethers, etc. Alcohols that can be used in the composition of the invention include methanol, ethanol, isopropanol, tertiary butanol, etc. Esters that can be used include amyl acetate, butyl acetate, ethyl acetate, esters of glycols, and others. Glycols and glycol ethers that are useful as solvents in the invention include ethylene glycol, propylene glycol, and oligomers and higher polymers of ethylene or propylene glycol in the form of polyethylene or polypropylene glycols. In solid organic concentrates the high molecular weight polymers are preferred.

The composition used for practicing the method of the invention can be formulated in solid form such as a cast solid, large granules or pellets. Such solid forms are typically made by combining the cellulase enzyme with a solidification agent and forming the combined material in a solid form. Both organic and inorganic solidification agents can be used. The solidification agents must be water soluble or dispersible, compatible with the cellulase enzyme, and easily used in manufacturing equipment.

Inorganic solid forming agents that can be used are typically hydratable alkali metal or alkaline earth metal inorganic salts that can solidify through hydration. Such compositions include sodium, potassium or calcium, carbonate, bicarbonate, triphosphosphate silicate, and other hydratable salts. The organic solidification agents typically include water soluble organic polymers such as polyethylene oxide or polypropylene oxide polymers having a molecular weight of greater than about 1,000, preferably greater than about 1,400. Other water soluble polymers can be used including polyvinyl alcohol, polyvinyl pyrrolidone, polyalkyl oxazolines, etc. The preferred solidification agent comprises a polymer of polyethylene oxide having an average molecular weight of greater than about 1,000 to about 20,000, preferably 1,200 to 10,000. Such compositions are commercially available as CARBOWAX® 1540, 4000, 6000. To the extent that the nonionic surfactants and other ingredients are soluble in solid polymer compositions, the solid organic matrices can be considered solvent.

Additionally, solid pellet-like compositions can be made by pelletizing the enzyme using well known pressure pelletizing techniques in which the cellulase enzyme in combination with a binder is compacted under pressure to a tablet

or pellet composition.

The compositions also contain 1-50 wt-%, preferably 5-30 wt-% of one or more alkali metal salts selected from the following compounds as the alkali or inorganic electrolyte: silicates, carbonates and sulfates. Further, the composition may contain organic alkalis such as triethanolamine, diethanolamine, monoethanolamine, and triisopropanolamine.

The cellulases are deactivated in some cases in the presence of heavy metal ions including copper, zinc, chromium, mercury, lead, manganese, or silver ions or their compounds. Various metal chelating agents and metal-precipitating agents are effective against these inhibitors. They include, for example, divalent metal ion sequestering agents as listed below with reference to optional additives as well as magnesium silicate and magnesium sulfate.

Cellulose, glucose and gluconolactone can act as an inhibitor. It is preferred to avoid the co-presence of these saccharides with the cellulase if possible. In case the co-presence is unavoidable, it is necessary to avoid the direct contact of the saccharides with the cellulase by, for example, coating them.

Long chain fatty acid salts and cationic surfactants act as the inhibitors in some cases. However, the co-presence of these substances with the cellulase is allowable if the direct contact of them is prevented by some means such as tableting or coating.

The above-mentioned masking agents and methods may be employed, if necessary, in the present invention.

The usable activators vary depending on variety of the cellulases. In the presence of proteins, cobalt and its salts, magnesium and its salts, and calcium and its salts, potassium and its salts, sodium and its salts or monosaccharides such as mannose and xylose, the cellulases are activated and their deterging powers can be improved.

The usable antioxidants include, for example, *tert*-butylhydroxytoluene, 4,4'-butylidenebis(6-*tert*-butyl-3-methylphenol), 2,2'-butylidenebis(6-*tert*-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1-bis(4-hydroxyphenyl)cyclohexane.

The usable solubilizers include, for example, lower alcohols such as ethanol, benzenesulfonate salts, lower alkyl-benzenesulfonate salts such as *p*-toluenesulfonate salts, glycols such as propylene glycol, acetylbenzenesulfonate salts, acetamides, pyridinedicarboxylic acid amides, benzoate salts and urea.

The compositions for use in practising the method of the present invention can be used in a broad pH range of about 6.5 to 10, preferably 6.5 to 8.

Solid concentrate compositions may contain 20-60 wt-% of one or more builder components selected from the group consisting of alkali metal salts and alkanolamine salts of the following compounds: phosphates such as orthophosphate, pyrophosphate, tripolyphosphate, metaphosphate, hexametaphosphate and phytic acid; phosphonates such as ethane-1,1-diphosphonate, ethane-1,1,2-triphosphonate, ethane-1-hydroxy-1,1-diphosphonate and its derivatives, ethanehydroxy-1,1,2-triphosphonate, ethane-1,2-dicarboxy-1,2-diphosphonate and methanehydroxyphosphonate; phosphonocarboxylates such as 2-phosphonobutane-1,2-dicarboxylate, 1-phosphonobutane-2,3,4-tricarboxylate and α -methylphosphonosuccinate; salts of amino acids such as aspartic acid, glutamic acid and glycine; aminopolycarboxylates such as nitrilotriacetate, ethylenediaminetetraacetate, diethylenetriaminepentaacetate, iminodiacetate, glycol ether diamine tetraacetate, hydroxyethyliminodiacetate and dienkolate; high molecular electrolytes such as polyacrylic acid, polyacetic acid, polyitaconic acid, polycitraconic acid, polyfumaric acid, polymaleic acid, polymaleic acid, polymaleic acid, poly- α -hydroxyacrylic acid, polyvinylphosphonic acid, sulfonated polymaleic acid, maleic anhydride/diisobutylene copolymer, maleic anhydride/styrene copolymer, maleic anhydride/methyl vinyl ether copolymer, maleic anhydride/ethylene copolymer, maleic anhydride/ethylene crosslinked copolymer, maleic anhydride/vinyl acetate copolymer, maleic anhydride/acrylonitrile copolymer, maleic anhydride/acrylic ester copolymer, maleic anhydride/butadiene copolymer, maleic anhydride/isoprene copolymer, poly- β -ketocarboxylic acid derived from maleic anhydride and carbon monoxide, itaconic acid/ethylene copolymer, itaconic acid/aconitic acid copolymer, itaconic acid/maleic acid copolymer, itaconic acid/acrylic acid copolymer, malonic acid/methylene copolymer, mesaconic acid/fumaric acid copolymer, ethylene glycol/ethylene terephthalate copolymer, vinylpyrrolidone/vinyl acetate copolymer, 1-butene-2,3,4-tricarboxylic acid/itaconic acid/acrylic acid copolymer, polyester polyaldehydocarboxylic acid containing quaternary ammonium group, *cis*-isomer of epoxy-succinic acid, poly[N,N-bis(carboxymethyl)acrylamide], poly(hydroxycarboxylic acid), starch/succinic acid or maleic acid or terephthalic acid ester, starch/phosphoric acid ester, dicarboxystarch, dicarboxymethylstarch, and cellulose/succinic acid ester; non-dissociating polymers such as polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone and cold water soluble, urethanated polyvinyl alcohol; and salts of dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and decane-1,10-dicarboxylic acid; salts of diglycolic acid, thiodiglycolic acid, oxalacetic acid, hydroxydisuccinic acid, carboxymethylhydroxysuccinic acid and carboxymethyltartronic acid; salts of hydroxycarboxylic acids such as glycolic acid, malic acid, hydroxypivalic acid, tartaric acid, citric acid, lactic acid, gluconic acid, mucic acid, glucuronic acid and dialdehydostarch oxide; salts of itaconic acid, methylsuccinic acid, 3-methylglutaric acid, 2,2-dimethylmalonic acid, maleic acid, fumaric acid, glutamic acid, 1,2,3-propanetricarboxylic acid, aconitic acid, 3-butene-1,2,3-tricarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, ethanetetracarboxylic acid, ethenetetracarboxylic acid, *n*-alkenylaconitic acid, 1,2,3,4-cyclopentanetetracarboxylic acid, phthalic acid, trimelic acid, hemimellitic acid, pyromellitic acid, benzenhexacarboxylic acid, tetrahydrofuran-1,2,3,4-tetracarboxylic acid and tetrahydrofuran-2,2,5,5-tetracarboxylic acid; salts of sulfonated carboxylic acids such as sulfoitaconic acid,

sulfotricarballylic acid, cysteic acid, sulfoacetic acid and sulfosuccinic acid; carboxymethylated sucrose, lactose and raffinose, carboxymethylated pentaerythritol, carboxymethylated gluconic acid, condensates of polyhydric alcohols or sugars with maleic anhydride or succinic anhydride, condensates of hydroxycarboxylic acids with maleic anhydride or succinic anhydride, and the like.

In somewhat greater detail, the clothing items can be contacted with an aqueous treatment solution containing cellulase enzyme and a surfactant to promote the action of the cellulase for a sufficient time to produce local variations in color density in the surface of the fabric. The amount of treatment solution used to treat the clothing items typically depends on the ratio of cellulase in the product and the dry weight of the clothing items to be washed. Typically the solutions used in the methods of the invention can contain a minimum of about 6,000 CMC units of cellulase per 0.45 kg of clothes, preferably 6,500 to 75,000 CMC units per 0.45 kg, most preferably 12,000 to 60,000 CMC units per 0.45 kg to obtain the "stone-washed" look.

The treatment solutions used to contact the clothes can typically have the following ingredients.

Table 1

Aqueous Treating Compositions

<u>Ingredient</u>	<u>Useful</u>	<u>Preferred</u>	<u>Most Preferred</u>
Cellulase	> 2,500	2,500-30,000	6,000-20,000
Enzyme Composition*			
Surfactant	about 0-1,000 ppm	10-900 ppm	15-750 ppm
Water	Balance	Balance	Balance

a

*Amounts in CMC units per liter.

Table 2

Concentrate Compositions			
Ingredient	Useful	Preferred	Most Preferred
Cellulase	1-90 wt-%	2-80 wt-%	5-75 wt-%
Enzyme composition Surfactant	99-0 wt-%	98-5 wt-%	95-10 wt-%
Solvent	Balance	Balance	Balance

Table 3

Inorganic Solid Concentrate			
Ingredient	Useful	Preferred	Most Preferred
Cellulase	25-90 wt-%	30-85 wt-%	35-80 wt-%
Enzyme Hydratable	20-60 wt-%	20-55 wt-%	25-50 wt-%
Inorganic Salt Buffer System Sequestrant	0-25 wt-%	5-20 wt-%	7-15 wt-%
Water of Hydration	Balance	Balance	Balance

Table 4
Organic Solid Concentrate

<u>Ingredient</u>	<u>Useful</u>	<u>Preferred</u>	<u>Most Preferred</u>
Cellulase	25-90 wt-%	30-85 wt-%	35-80 wt-%
Enzyme			
Surfactant	99-0 wt-%	98-5 wt-%	95-10 wt-%
PEG*	20-60 wt-%	20-55 wt-%	25-50 wt-%
Sequestrant	0-25 wt-%	5-20 wt-%	7-20 wt-%
Buffer System	0-5 wt-%	1-4 wt-%	1.5-3.5 wt-%

* PEG = polyethylene oxide (M.W. 1,000-9,000).

The compositions are typically diluted in water in household, institutional, or industrial machines having a circular drum held in a horizontal or vertical mode in order to produce the "stone-washed" appearance without the use of pumice or other particulate abrasive. Most commonly the denim or other fabric clothing items are added to the machine according to the machine capacity per the manufacturer's instructions. Typically the clothes are added prior to introducing water into the drum but the clothes can be added to water in the machine or to the pre-diluted treatment composition. The clothing is contacted with the treatment composition and agitated in the machine for a sufficient period to ensure that the clothing has been fully wetted by the treatment composition and to ensure that the cellulase enzyme has had an opportunity to cleave cellulose in the fabric material. At this time if the treatment composition is to be reused, it is often drained from the tub and saved for recycle. If the treatment composition is not to be reused, it can remain on the clothing for as long as needed to produce color variation. Such treatment periods are greater than 5 minutes, greater than 30 minutes and up to 720 minutes, depending on amount of enzyme, during all or part of the mechanical machine action used to produce in the cellulase treated fabric the variations in color density. We believe that there is an interaction between the cellulase modified fabric and mechanical tumbling or action which removes cellulose from the fabric surface and the indigo dye to create a variation in color density from place to place on fabric panels and seams. Further, the action of the enzyme appears to cause puckering in the seams and a creation of a soft, wrinkled look in fabric panels.

The following Examples provide specific details with respect to the methods of the invention and include a best mode.

Examples I-III

Into a Milnor 16 kg (35 lb.) capacity washing machine was placed new blue denim jeans and into the machine was placed 95 l (25 gallons) of 50°C (120° F.) water containing an amylase enzyme desizing stripper composition. The contents of the machine was agitated for 9 minutes and the aqueous solution was dumped. Into the machine was placed 95 l (25 gallons) of water at 50°C (120° F.) containing an amount of cellulase enzyme (see Table 5 below) and 10 milliliters of a sour, soft softening agent comprising an aqueous solution containing 23 wt-% H_2SiF_6 and 50 wt-% citric acid. The jeans were agitated in the cellulase composition for 1 hour and the aqueous composition was dumped. The jeans were then rinsed in cold water and in three successive hot water rinses at 50°C (120° F.), 43°C (110° F.), and a final rinse at 38°C (100° F.) containing 5 milliliters of the sour soft product.

Table 5

<u>Example</u>	<u>Concentrate</u>	<u>CMCU/L*</u>	<u>CMCU/LB*</u>		<u>Grams/</u>
	<u>Grams/L</u>	<u>6,000</u>	<u>Pair</u>	<u>Pair</u>	<u>Pair</u>
I	200	7,459	32,000	48,000	20
II	300	11,189	48,000	72,000	30
III	400	14,918	64,000	96,000	40

 * Carboxymethyl cellulose units

Table 6

Visible Spectrophotometer Scan of
Stone Washed Jeans and Product of Example II

<u>Wave</u>	<u>Stone</u>	<u>Example II</u>	<u>Differences</u>
<u>Length</u>	<u>Washed Jeans</u>		
380	11.50	11.01	-0.49
390	15.71	15.32	-0.39
400	18.57	18.49	-0.08
410	21.70	21.99	0.69
420	23.01	24.22	1.20
430	22.96	24.24	1.28
440	22.19	23.53	1.34
450	21.31	22.62	1.31
460	20.38	21.64	1.26
470	19.43	20.63	1.20
480	18.60	19.71	1.10
490	17.91	18.92	1.01
500	17.18	18.08	0.90
510	16.35	17.13	0.77
520	15.40	16.06	0.66
530	14.40	14.92	0.52
540	13.47	13.88	0.41

EP 0 307 564 B1

	550	12.77	13.08	0.31
	560	12.32	12.60	0.28
5	570	11.94	12.15	0.21
	580	11.42	11.59	0.17
	590	10.85	10.97	0.12
10	600	10.35	10.39	0.04
	610	9.95	9.94	-0.01
	620	9.60	9.56	-0.04
	630	9.15	9.07	-0.08
15	640	8.75	8.64	-0.11
	650	8.44	8.30	-0.14
	660	8.35	8.21	-0.14
20	670	8.66	8.58	-0.08
	680	9.70	9.73	0.03
	690	11.83	12.12	0.29
25	700	15.83	16.60	0.77
	710	22.62	23.99	1.37
	720	32.13	33.84	1.71
30	730	42.55	43.96	1.41
	740	51.26	51.92	0.65
	750	57.04	57.03	-0.01

35

Detailed Discussion of the Drawings

Fig. 1 is a graphical representation of the data in the above table. The graph appears to be a single line consisting of dots and dashes, however the graph shows that the percent reflectance of the stone washed denims and the denims produced using the compositions and methods of this invention are virtually identical. The differences shown in column 4 of the above table indicate that at certain wavelengths minor differences occur, however the curves are virtually superimposable.

Claims

1. A method of forming, in unsewn dyed cellulosic fabric or a newly manufactured garment made of a dyed cellulosic fabric a distressed appearance substantially the same as that produced by conventional pumice stone processing, which method comprises:

50

(1) contacting the fabric or the garment with an aqueous composition consisting essentially of:

- (a) a major proportion of water;
- (b) at least about 2,500 CMC units of a cellulase enzyme composition per liter of aqueous composition;
- (c) about 0 to 1000 parts of an enzyme-compatible surfactant per one million parts of the aqueous composition; and

55

(2) agitating the enzyme-treated fabric or garment for a time sufficient for forming localized areas of variation

EP 0 307 564 B1

in color density through the removal of dye from the fabric.

2. The method of claim 1 wherein after the fabric or the garment is contacted with the aqueous composition, but before agitation, the aqueous solution is removed from contact with the fabric or garment.
3. The method of claim 1 wherein the fabric or the garment is contacted with the aqueous solution for at least 5 minutes.
4. The method of claim 1 wherein the fabric or the garment is agitated for 30 to 720 minutes.
5. The method of claim 1 wherein the cellulase is a fungal cellulase.
6. The method of claim 1 wherein the fabric is indigo dyed denim.
7. The method of claim 1 wherein the surfactant is a polymeric nonionic surfactant derived from repeated units of ethylene oxide, propylene oxide or mixtures thereof, and is present at a concentration of 5 to 800 parts of surfactant per one million parts of aqueous composition.
8. The method of claim 7 wherein the composition comprises an alkylphenol alkoxylate or an aliphatic alcohol alkoxylate.
9. The method of any of the preceding claims which method comprises:
 - (1) contacting the fabric or garment in a circular drum machine with an aqueous composition, derived from a solid concentrate, said aqueous composition consisting essentially of:
 - (a) a major proportion of water;
 - (b) about 6,000 to 75,000 CMC units of a cellulase enzyme composition per 0.45 kg of fabric; and
 - (c) at least about 2,500 CMC units of cellulase enzyme per liter of the aqueous composition; and
 - (2) agitating the enzyme-treated fabric or garment.
10. The method of claim 9 wherein the aqueous composition additionally comprises a nonionic surfactant.

Patentansprüche

1. Verfahren zur Erzeugung eines abgenutzten Aussehens, das im wesentlichen dem Aussehen entspricht, welches mittels eines herkömmlichen Bimstein-Verfahrens erzeugt wird, bei ungenähtem gefärbten Zellulosegewebe oder bei einem aus Zellulosegewebe neu hergestellten Bekleidungsstück, wobei das Verfahren umfaßt:
 - (1) Inkontaktbringen des Gewebes oder Bekleidungsstückes mit einer wässrigen Zusammensetzung, die im wesentlichen besteht aus:
 - (a) einem Hauptanteil an Wasser;
 - (b) zumindest ungefähr 2.500 CMC-Einheiten einer Cellulaseenzym-Zusammensetzung je Liter wässriger Zusammensetzung;
 - (c) ungefähr 0 bis 1000 Teile eines enzymverträglichen oberflächenaktiven Stoffes je eine Million Teile der wässrigen Zusammensetzung; und
 - (2) ausreichend langes Bewegen des Enzym-behandelten Gewebes oder Bekleidungsstücks, um durch die Entfernung von Farbstoff von dem Gewebe lokale Bereiche unterschiedlicher Farbdichte zu erzeugen.
2. Verfahren nach Anspruch 1, wobei, nachdem das Gewebe oder das Bekleidungsstück mit der wässrigen Zusammensetzung in Kontakt gebracht wurde, aber vor dem Bewegen, die wässrige Lösung außer Kontakt mit dem Gewebe oder dem Bekleidungsstück gebracht wird.
3. Verfahren nach Anspruch 1, wobei das Gewebe oder das Bekleidungsstück mit der wässrigen Lösung für zumindest 5 Minuten in Kontakt gebracht wird.

EP 0 307 564 B1

4. Verfahren nach Anspruch 1, wobei das Gewebe oder das Bekleidungsstück für 30 bis 720 Minuten bewegt wird.
5. Verfahren nach Anspruch 1, wobei die Zellulase eine Pilzzellulase ist.
- 5 6. Verfahren nach Anspruch 1, wobei das Gewebe indigogefärbter Jeansstoff ist.
7. Verfahren nach Anspruch 1, wobei der oberflächenaktive Stoff ein polymerer nichtionischer oberflächenaktiver Stoff ist, abgeleitet von wiederholenden Einheiten aus Ethylenoxid, Propylenoxid oder Mischungen davon, und in einer Konzentration von 5 bis 800 Teile oberflächenaktiver Stoff je eine Million Teile wässriger Zusammensetzung vorliegt.
- 10 8. Verfahren nach Anspruch 7, wobei die Zusammensetzung ein Alkylphenolalkoxylat oder ein aliphatisches Alkoholalkoxylat umfaßt.
9. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Verfahren umfaßt:
 - 15 (1) Inkontaktbringen des Gewebes oder Bekleidungsstücks, in einer Kreistrommelmaschine, mit einer wässrigen Zusammensetzung, erhalten aus einem Feststoffkonzentrat, worin die wässrige Zusammensetzung im wesentlichen besteht aus:
 - 20 (a) einem Hauptanteil an Wasser;
 - (b) ungefähr 6.000 bis 75.000 CMC-Einheiten einer Zellulaseenzym-Zusammensetzung je 0,45 kg Gewebe; und
 - (c) zumindest ungefähr 2.500 CMC-Einheiten Zellulaseenzym je Liter der wässrigen Zusammensetzung; und
 - 25 (2) Bewegen des Enzym-behandelten Gewebes oder Bekleidungsstücks.
10. Verfahren nach Anspruch 9, worin die wässrige Zusammensetzung zusätzlich einen nichtionischen oberflächenaktiven Stoff umfaßt.

Revendications

1. Procédé pour produire sur un tissu cellulosique teint sans couture, ou un vêtement nouvellement fabriqué fait en tissu cellulosique teint, un aspect vieilli sensiblement identique à celui qu'on obtient par traitement conventionnel à la pierre ponce, lequel procédé consiste à :
 - 35 (1) mettre en contact le tissu ou le vêtement avec une composition aqueuse essentiellement constituée de :
 - 40 (a) une majeure proportion d'eau ;
 - (b) au moins environ 2500 unités CMC d'une composition d'enzyme cellulase par litre de composition aqueuse ;
 - (c) environ 0 à 1000 parties d'un tensioactif compatible avec l'enzyme pour un million de parties de la composition aqueuse ; et
 - 45 (2) agiter le tissu ou le vêtement traité à l'enzyme pendant un laps de temps suffisant pour former des zones localisées de variation de densité de couleur du fait de l'élimination du colorant du tissu.
2. Procédé selon la revendication 1, dans lequel, après la mise en contact du tissu ou du vêtement avec la composition aqueuse, mais avant l'agitation, on interrompt le contact entre la solution aqueuse et le tissu ou le vêtement.
3. Procédé selon la revendication 1, dans lequel le tissu ou le vêtement est mis en contact avec la solution aqueuse pendant au moins 5 minutes.
- 55 4. Procédé selon la revendication 1, dans lequel le tissu ou le vêtement est agité pendant 30 à 720 minutes.
5. Procédé selon la revendication 1, dans lequel la cellulase est une cellulase fongique.

EP 0 307 564 B1

6. Procédé selon la revendication 1, dans lequel le tissu est un denim teint en indigo.

7. Procédé selon la revendication 1, dans lequel le tensioactif est un tensioactif non-ionique polymère dérivé d'unités répétées d'oxyde d'éthylène, d'oxyde de propylène ou de mélanges de ceux-ci, et est présent à une concentration de 5 à 800 parties de tensioactif pour un million de parties de composition aqueuse.

8. Procédé selon la revendication 7, dans lequel la composition comprend un alkylphénol alcoxylé ou un alcool aliphatique alcoxylé.

9. Procédé selon l'une quelconque des revendications précédentes, lequel procédé consiste à :

(1) mettre en contact le tissu ou le vêtement, dans une machine à tambour circulaire, avec une composition aqueuse dérivée d'un concentré solide, ladite composition aqueuse étant essentiellement constituée de :

(a) une majeure proportion d'eau ;

(b) environ 6000 à 75000 unités CMC d'une composition d'enzyme cellulase pour 0,45 kg de tissu ; et

(c) au moins environ 2500 unités CMC d'enzyme cellulase par litre de la composition aqueuse ; et

(2) agiter le tissu ou le vêtement traité à l'enzyme.

10. Procédé selon la revendication 9, dans lequel la composition aqueuse comprend de plus un tensioactif non-ionique.

VISUAL
SPECTRO PHOTO METRIC
COMPARISON OF STONE-WASHED
JEANS AND JEANS OF THE INVENTION

..... PRODUCT OF EXAM.II

----- STANDARD STONE-
WASHED JEANS

